

He(I) AND He(II) PHOTOELECTRON SPECTRA OF MONONUCLEAR TRANSITION METAL CARBONYL COMPLEXES CONTAINING A 1,4-DIAZA-1,3-BUTADIENE LIGAND *

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Summary

He(I) and He(II) photoelectron spectra have been recorded for the following mononuclear transition metal carbonyl complexes containing symmetrically 1,4-disubstituted 1,4-diaza-1,3-butadienes, $\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}$, d^6 [$\text{M}(\text{CO})_4(\text{RN}=\text{CHCH}=\text{NR})$] ($\text{M} = \text{Cr}, \text{W}, \text{R} = i\text{-Pr}$; $\text{M} = \text{Mo}, \text{R} = t\text{-Bu}$) and [$\text{ReCl}(\text{CO})_3(i\text{-Pr}-\text{N}=\text{CHCH}=\text{N}-i\text{-Pr})$], d^8 [$\text{M}(\text{CO})_3(\text{RN}=\text{CR}'\text{CR}''=\text{NR})$] ($\text{M} = \text{Fe}, \text{R} = t\text{-Bu}, n\text{-Bu}, c\text{-Hex}, \text{R}' = \text{R}'' = \text{H}$; $\text{M} = \text{Fe}, \text{R} = n\text{-Bu}, \text{R}' = \text{R}'' = \text{Me}$; $\text{M} = \text{Ru}, \text{R} = i\text{-Pr}_2\text{CH}, \text{R}' = \text{R}'' = \text{H}$) and [$\text{Fe}(t\text{-BuN}=\text{CHCH}=\text{N}-t\text{-Bu})_2$], and d^{10} [$\text{Ni}(\text{CO})_2(t\text{-BuN}=\text{CHCH}=\text{N}-t\text{-Bu})$] and [$\text{Ni}(t\text{-BuN}=\text{CHCH}=\text{N}-t\text{-Bu})_2$].

The observed vertical ionization energies (IE 's) are tabulated and assigned to metal d orbitals and ligand systems on the basis of the results of semi-empirical molecular orbital (MO) calculations, He(I)/He(II) intensity ratios, and comparisons with related molecules (trend effects). The weighted average IE of the metal d orbitals in each R-DAB complex (\overline{IE}'_d) is lower than that of the corresponding unsubstituted metal carbonyl complex (\overline{IE}_d). The values of $\Delta IE_d (= \overline{IE}'_d - \overline{IE}_d)$ are -1.54 eV for the d^6 complexes, -1.80 eV for the d^8 system and -2.09 eV for the d^{10} compound. This means that ΔIE_d increases by the same amount on going from d^6 to d^8 complexes (0.26 eV) as it does on going from d^8 to d^{10} complexes (0.29 eV). Replacement of two CO groups by a second $\text{RN}=\text{CHCH}=\text{NR}$ ligand leads to a further lowering of the weighted average IE of the d orbitals (-0.5 eV) which is significantly less than that found for the first substitution.

* Most known 1,4-diaza-1,3-butadienes have the general formula $\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}$ and herein this will be abbreviated to R-DAB {R', R''}. The important subgroup of this class is $\text{RN}=\text{CHCH}=\text{NR}$ (R-DAB{H,H}), but for economy of space if the R grouping is specifically stated then the form R substituent-DAB is used and this implies proton substitution at the α -diimine carbon atoms, e.g. $t\text{-Bu}-\text{N}=\text{CHCH}=\text{N}-t\text{-Bu}$ become $t\text{-Bu}$ -DAB. Other important abbreviations for the R groups used throughout this paper are Me = methyl, Et = ethyl, $i\text{-Pr}$ = iso-propyl, $t\text{-Bu}$ = tert. butyl, $i\text{-Pr}_2\text{CH}$ = 2,4-di-isopropyl methyl, $c\text{-Hex}$ = cyclohexyl, $n\text{-Bu}$ = n-butyl, Mes = mesityl, $p\text{-Tol}$ = p -tolyl [1].

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Introduction

In the last decade there has been considerable interest in the inorganic and organometallic chemistry of 1,4-diaza-1,3-butadiene ($\text{RN}=\text{C}(\text{R}')\text{C}(\text{R}'')=\text{NR}$), represented subsequently as R-DAB (R',R'') [1] and the related ligands 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) (see Fig. 1, A–C) [2]. Compared to the last two ligands, R-DAB exhibits a greater variety of bonding modes. Thus, apart from σ -bonding to both transition and non-transition metals [1–4], favoured by the presence of a symmetric (n_+) and an anti-symmetric (n_-) lone pair combination, π -bonding via its π -type orbitals (π_2^-) [5] and also a combination of these bonding modes have been observed. The different bonding modes, σ -N monodentate (D) [6a], σ -N, σ -N' bridging (E) [6b], σ -N, σ -N' bidentate (F) [1], σ -N, σ -N', η^2 -C=N (G) [1,2a,7,8a] and σ -N, σ -N', η^2 -C=N, η^2 -C=N' (H) [1,8b–e] are shown schematically in Fig. 1.

Recently the organometallic radicals [$\text{RZn}(\text{t-Bu-DAB}^\cdot)$] ($\text{R} = \text{Me}, \text{Et}$) and [$\text{Et}_2\text{Al}(\text{t-Bu-DAB}^\cdot)$] were reported [9] and, with the aid of ultraviolet photoelectron spectroscopy (UPS), the ionization energy of the radical electron, residing mainly in the normally empty LUMO, was found to be 6 eV [10]. The low energy of this LUMO is responsible for the strong π -backbonding in type F (Fig. 1) complexes and also for their low-energy metal to ligand charge transfer (MLCT) transitions. The MLCT photochemistry and photophysics of a series of R-DAB complexes has been studied by us in relationship to their resonance Raman (rR) spectra. Results of these studies have been published for the complexes [$\text{M}(\text{CO})_4(\text{R-DAB})$] ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [2b,11,12], [$\text{M}(\text{CO})_3(\text{R-DAB})$] ($\text{M} = \text{Fe}, \text{Ru}$) [13–15] and [$\text{MX}(\text{CO})_3(\text{R-DAB})$] ($\text{M} =$

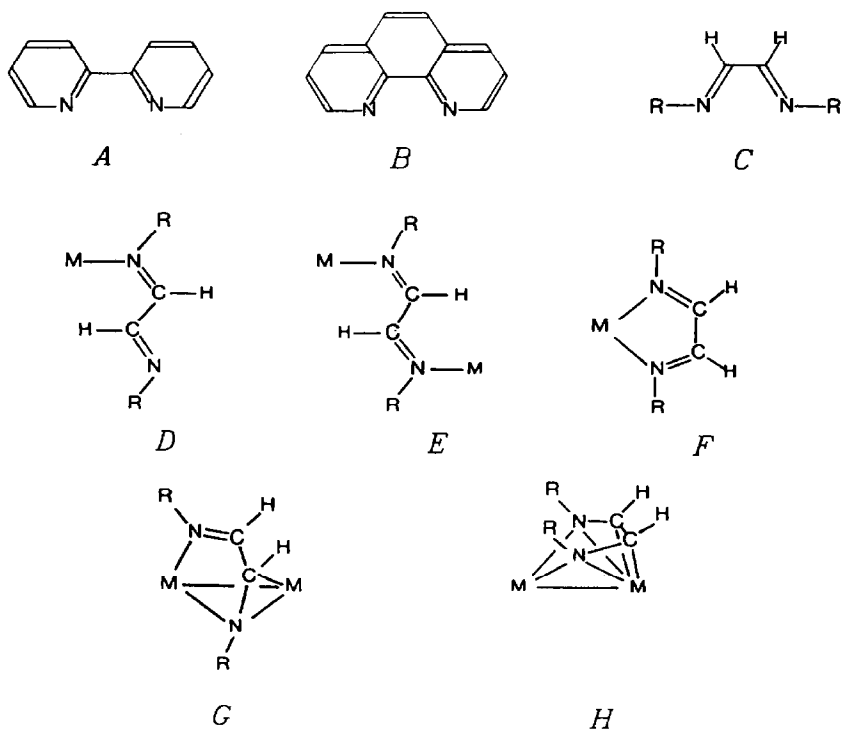


Fig. 1. Structures of some α -diimines (A–C) and bonding modes of R-DAB to (transition) metals.

Mn, Re; X = Cl, Br) [2a,16]. During these photochemical investigations we needed more detailed information concerning the electronic structures of these complexes in their ground states. (The natures of the excited states can be derived from the rR spectra.) Because of this we undertook a detailed UPS study of 1,4-diaza-1,3-butadiene complexes with d^6 , d^8 and d^{10} transition metals.

Experimental

Syntheses

The complexes $[\text{Cr}(\text{CO})_4(\text{i-Pr-DAB})]$, $[\text{Mo}(\text{CO})_4(\text{t-Bu-DAB})]$, $[\text{W}(\text{CO})_4(\text{i-Pr-DAB})]$ [1,2b,3a], $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ [2a], $[\text{Fe}(\text{CO})_3(\text{R-DAB}\{\text{R}',\text{R}''\})]$ (R = t-Bu, c-Hex, R' = R'' = H; R = n-Bu, R' = R'' = Me) [3a,4,7], $[\text{Ru}(\text{CO})_3(\text{i-Pr}_2\text{CH-DAB})]$ [17], $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$ [3a,18], $[\text{Ni}(\text{t-Bu-DAB})_2]$ [19] and $[\text{Fe}(\text{t-Bu-DAB})_2]$ [20] were prepared by published methods. The compounds were identified by ^1H NMR, FT-IR and elemental analyses. The thermal stabilities in the gas phase were checked by thermoanalyses under high vacuum conditions.

Photoelectron spectra

The UP spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer, equipped with a Helectros Developments hollow cathode He(I)/He(II) light source. The spectra were calibrated against Ar and Xe as internal references.

Air-sensitive compounds were loaded into the sample holder in a N_2 glove box.

Results and discussion

d^6 Complexes

(i) $[\text{M}(\text{CO})_4(\text{R-DAB})]$ ($M = \text{Cr}, \text{W}, \text{R} = \text{i-Pr}; M = \text{Mo}, \text{R} = \text{t-Bu}$)

The expanded He(I) and He(II) photoelectron (PE) spectra of $[\text{W}(\text{CO})_4(\text{i-Pr-DAB})]$ and the (expanded) He(I) low IE region of the corresponding Cr complex are shown in Fig. 2. These data, together with those for the Mo complex, are listed in Table 1.

The assignments of the spectra can be made with the aid of (i) He(I)/He(II) intensity ratios, (ii) semi-empirical MO MNDO [21] calculations on the model ligand Me-DAB, and (iii) CNDO/S [22] calculations on the Cr complex. The results of these calculations, using Koopmans' Theorem [23], are presented in Table 2, and compared with the experimental IE 's.

A qualitative MO scheme (interaction diagram) can be constructed using the calculated results of Table 2, the theoretical work on $\text{Cr}(\text{CO})_4$ moieties by Elian and Hoffmann [24], and the electronic absorption [2b,11] and resonance Raman results obtained by Balk et al. [12].

The UP spectra of these d^6 complexes can be divided into three regions: a sharp band (A) at ~ 7 eV, two overlapping broad bands at 9–11 eV (B + C), and a complex region above 12 eV containing ionizations from inner lying orbitals of the R-DAB ligand and CO. As usual for zerovalent d^6 complexes, the UP spectra show a narrow band arising from ionizations from closely spaced transition metal d orbitals [25–27]. Band A shows an increase of cross-section relative to B and C on going from He(I) to He(II) radiation, which is quite common for transition metal

complexes [25–27]. A is therefore assigned to the filled “ t_{2g} -like” metal d orbitals $a_1(d_{x^2-y^2})$, $b_2(d_{yz})$ and $a_2(d_{xy})$, respectively. A stabilization is observed for these metal d ionizations on going from Cr to W, since in the tungsten complexes the outermost electrons experience a decreased shielding from the metal nucleus. This phenomenon also leads to the greater electronegativity of W [28].

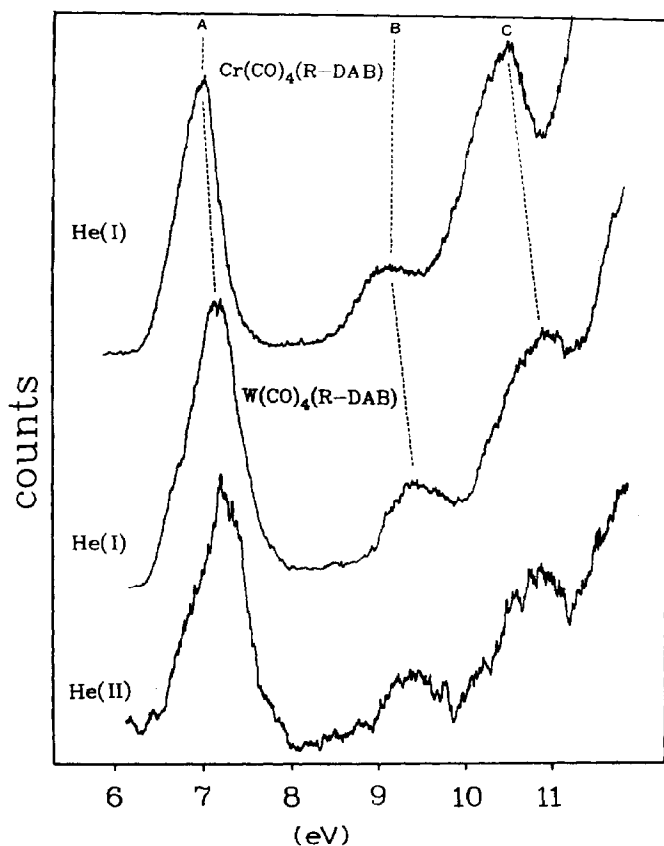


Fig. 2. Expanded He(I) photoelectron spectrum of $[\text{Cr}(\text{CO})_4(\text{R-DAB})]$ and of $[\text{W}(\text{CO})_4(\text{R-DAB})]$ ($\text{R} = \text{i-Pr}$).

TABLE 1

OBSERVED VERTICAL IONIZATION ENERGIES (eV) OF $[\text{M}(\text{CO})_4(\text{R-DAB})]$

M	R	$IE (\pm 0.05 \text{ eV})$		
		Band index		
		A	B	C
Cr	i-Pr	6.86	9.33	10.68
Mo	t-Bu	6.89	9.40	10.46
W	i-Pr	(6.73)7.12	9.44	10.82
Assignment		$d_{x^2-z^2}, d_{yz}, d_{xy}$	n_+	π_2^-
T_i		a_1, b_2, a_2	a_1	a_2

In the spectra of $[\text{W}(\text{CO})_4(\text{i-Pr-DAB})]$, band A exhibits a shoulder at ~ 6.7 eV on its lower *IE* side, which suggests the presence of spin-orbit (S-O) coupling. Although S-O coupling, which is one of the relativistic effects for heavy atoms [29,30], is formally forbidden (in first order [31,32]) for these complexes due to their

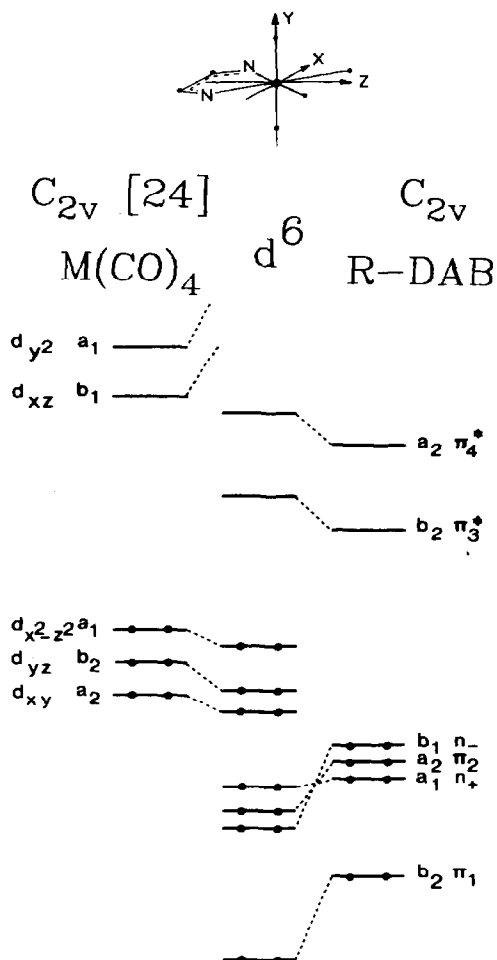


Fig. 3. Qualitative MO scheme of $[\text{M}(\text{CO})_4(\text{R-DAB})]$ complexes.

TABLE 2

A COMPARISON OF CALCULATED CNDO/S EIGENVALUES AND OBSERVED *IE*'S FOR $[\text{Cr}(\text{CO})_4(\text{R-DAB})]$

<i>IE</i> (eV) R = i-Pr	$-\epsilon_j$ (eV)		Assignment	
	R = H		$C_{2v} T_i$	Band index
6.86	9.14		$b_2 (d_{yz})$	A
	9.26		$a_2 (d_{xy})$	
	9.81		$a_1 (d_{x^2-z^2})$	
9.33	13.13		$a_1 (n_+)$	B
10.68	12.56		$a_2 (\pi_2^-)$	C

low symmetry (C_{2v}), such an effect is still observed in the absorption and luminescence spectra of e.g. $[\text{W}(\text{CO})_4(\text{ethylenediamine})]$ [33] and $[\text{W}(\text{CO})_4(\text{i-Pr-DAB})]$ [34]. The S–O splitting can be explained by assuming local C_{4v} symmetry for the d orbitals of W.

The second band **B** at ~ 9.5 eV is assigned to ionizations from the n_+ lone pair combination and the third one **C** to the $\pi_2(-)$ and probably n_- of the R-DAB ligand. The conclusion is based on the fact that the different intensity ratios in the He(I) and the He(II) spectra indicate greater $N_{2s/2p}$ participation in the second band **B**. Compared with the free ligand, the $\pi_2(-)$ orbital is stabilized as a result of σ -donation of the n_- to the metal centre. The π -backbonding into the empty π_3^* R-DAB orbital results in a stabilization of the d_{xy} and d_{yz} orbitals (Fig. 3).

Bands at higher IE are due to ionizations from $\pi_1(+)$ and σ orbitals of the R-DAB system and from 5σ , 1π and 4σ orbitals of the CO.

(ii) $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$

Extensive studies of the thermal stabilities of a series of $[\text{MX}(\text{CO})_3(\text{R-DAB})]$ ($X = \text{Cl}, \text{Br}$; $M = \text{Mn}, \text{Re}$) complexes showed that only $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ has sufficient vapour pressure at ca. $160^\circ\text{C}/10^{-6}$ torr to provide reliable UP spectra. Other compounds of the $[\text{MX}(\text{CO})_3(\text{R-DAB})]$ series showed either decomposition or a low sublimation rate over a large temperature range, typically $> 20^\circ\text{C}$ ($> 250^\circ\text{C}$) [35]. The He(I) and He(II) PE spectra of $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ are shown in Fig. 4, and the data are listed in Table 3 together with relevant data for related complexes. Assignments of the spectra have been made with the aid of cross-section differences, intensity ratios, and data for related complexes.

Before discussing the spectra it is worthwhile making a comparison between the level diagrams of $[\text{M}(\text{CO})_6]$ ($M = \text{Cr}, \text{Mo}, \text{W}$), $[\text{MCl}(\text{CO})_5]$ and $[\text{MCl}(\text{CO})_3(\text{R-DAB})]$

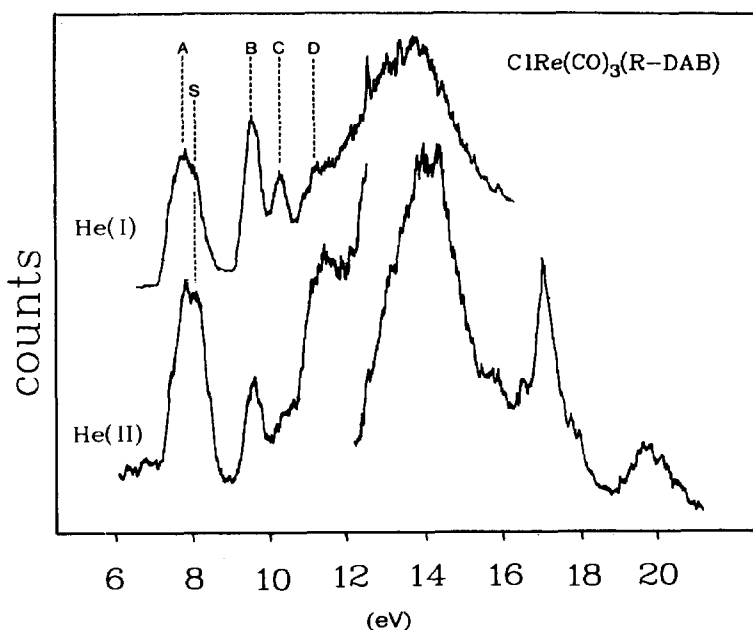


Fig. 4. He(I) and He(II) phototelectron spectra of $[\text{ReCl}(\text{CO})_3(\text{R-DAB})]$ ($\text{R} = \text{i-Pr}$).

($M = \text{Mn, Re}$) (restricted to the metal d^6 and chloride levels). The IE 's of the metal " t_{2g} " orbitals of $[\text{Cr}(\text{CO})_4(\text{i-Pr-DAB})]$ (see above) are destabilized by about 1.5 eV with respect to $[\text{Cr}(\text{CO})_6]$, indicating that substitution of two CO's by a R-DAB ligand, increases the electron-density on the metal centre. A similar destabilization of metal d orbitals (e and b_2 in the case $[\text{MCl}(\text{CO})_5]$) is expected on going from $[\text{MCl}(\text{CO})_5]$ to $[\text{MCl}(\text{CO})_3(\text{R-DAB})]$. Besides, this substitution of CO by R-DAB will also influence the energy separation between the metal d orbitals. Thus, for the complexes $[\text{ML}(\text{CO})_5]$ ($M = \text{Cr, W}$; $L = \text{NR}_3, \text{pyridine, PR}_3, \text{SR}_2$ etc.) [25,26], it was found that especially the metal e -level was sensitive to the nature of L , since the b_2 orbital only interacts with the π MO of the carbonyls whereas the e -level interacts

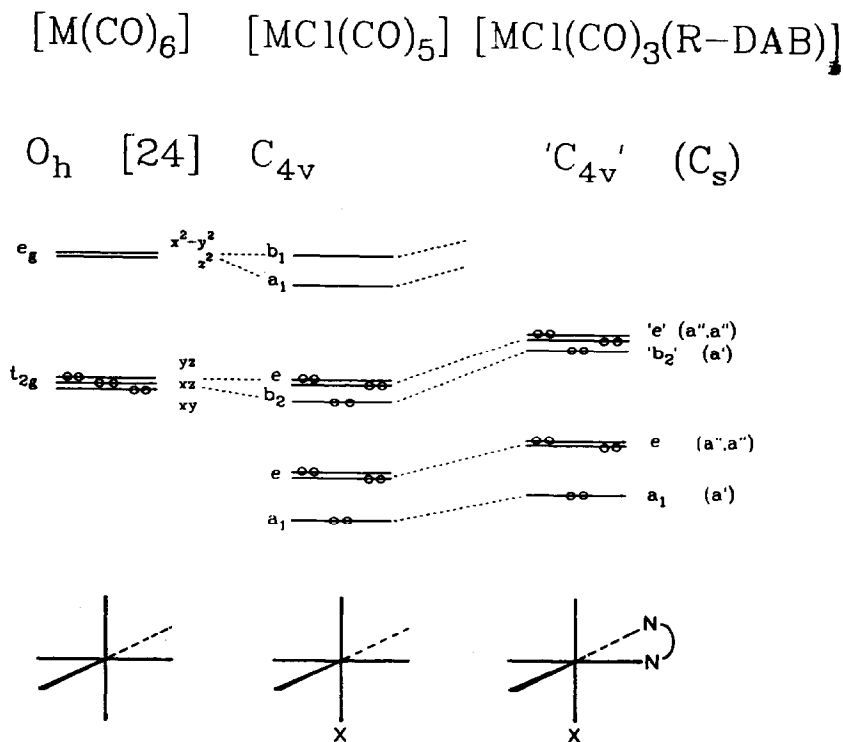


Fig. 5. Qualitative MO scheme of $[\text{MCl}(\text{CO})_3(\text{R-DAB})]$ complexes.

TABLE 3

OBSERVED VERTICAL IONIZATION ENERGIES (eV) OF $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ TOGETHER WITH UP DATA OF THE RELATED COMPOUND $[\text{ReCl}(\text{CO})_5]$

$IE (\pm 0.05 \text{ eV})$		Assignment	
$[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$	$[\text{ReCl}(\text{CO})_5]$ [25]		
7.76	8.80	metal d " e "	d_{xz}
	9.04	(S-O)	d_{yz}
	9.86	" b_2 "	d_{xy}
9.59	10.76	Cl lone pair	" e "
10.36	11.21	Cl lone pair	" a_1 "

with both L and CO π -orbitals. A π -acceptor ligand L stabilizes the e -level, causing a decrease of the e - b_2 energy separation [36].

For $[\text{ReCl}(\text{CO})_5]$ the e - b_2 separation was found to be 0.96 eV, the spin-orbit coupling ξ_{5d} of the Re e -level ($e'' + e'$) 0.24 eV (see Table 3), and the energy separation between the chloride levels e and a_1 0.45 eV [32].

The assignment of the spectrum of $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ is now straightforward (Table 3). A broad band (**A**) at ~ 7.7 eV has a shoulder (**S**) on its high IE side. Bands (**B**) and (**C**) have an intensity ratio of ca. 2/1 and an energy separation of 0.77 eV. Bands at higher energies are left out the discussion because of their complexity. With the aid of the He(II) PE spectrum it can be concluded that band **A** consist of ionizations from Re $5d$ orbitals, while band **B** and **C** arise from ionizations from chloride orbitals, these latter bands decreasing in cross-section relatively to **A** on going from He(I) to He(II) radiation [37]. Thus, band **A** arises from ionizations from the " e " and " b_2 " metal d orbitals of rhenium, and are indeed destabilized by about 1.47 eV with respect to $[\text{ReCl}(\text{CO})_5]$. As a result of the R-DAB substitution, there is hardly any separation left between " e " and " b_2 " levels. Also no spin-orbit coupling is observed for Re " e " level because of the low C_s symmetry of the complex, although it must be appreciated that the value of ξ is already small for $[\text{ReCl}(\text{CO})_5]$.

Because of the small cross-sections of band **B** and **C** in He(II) and their intensity ratio of ca. 2/1 in the He(I) spectrum, these bands are assigned to the " e " and " a_1 " chloride orbitals respectively. It is also clear from the large intensity decrease of band **C** in the He(II) spectrum that the e -level (band **B**) possesses more metal d character than the a_1 -level (band **C**).

The IE values of " e " and " a_1 " are destabilized with respect to those of $[\text{ReCl}(\text{CO})_5]$ (Table 3). This is also the result of introducing a R-DAB ligand, which increases not only the charge on the metal centre, but also that on the other ligands, CO and Cl. The destabilization of the " e " level is 1.20 eV, which is larger than that of the corresponding a_1 -level (0.85 eV). Ionization from the R-DAB ligand in $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$ are expected to be more or less the same as those for $[\text{Cr}(\text{CO})_4(\text{i-Pr-DAB})]$. The bands corresponding to n_+ and π_2 orbitals of these complexes have very small cross-sections (Fig. 2), and may therefore be obscured by chloride ionizations in the case of $[\text{ReCl}(\text{CO})_3(\text{i-Pr-DAB})]$.

d^8 Complexes

$[M(\text{CO})_3(\text{R-DAB}\{R',R''\})]$ ($M = \text{Fe}$, $R = \text{alkyl}$, $R' = R'' = \text{H}$ or Me ; $M = \text{Ru}$, $R = \text{i-Pr}_2\text{CH}$, $R' = R'' = \text{H}$)

The He(I) and He(II) PE spectra of $[\text{Fe}(\text{CO})_3(\text{t-Bu-DAB})]$ and $[\text{Ru}(\text{CO})_3(\text{i-Pr}_2\text{CH-DAB})]$ are shown in Figs. 6 and 7, respectively. Vertical ionization energies for these two compounds and their derivatives are listed in Table 4 together with their assignments, which will be discussed below.

The spectra can be divided into three regions: The 6–8 eV region contains two distinct bands (**A** and **B**), with a shoulder (**S**) at 7.46 eV, which is clearly visible in the expanded He(I) PE spectrum of $[\text{Fe}(\text{CO})_3(\text{t-Bu-DAB})]$. The second region (8–10 eV) contains just one band (**C**) at ~ 9 eV, and the third region (> 11 eV) contains many overlapping bands arising from the ionizations from inner lying σ orbitals of the ligand and CO groups.

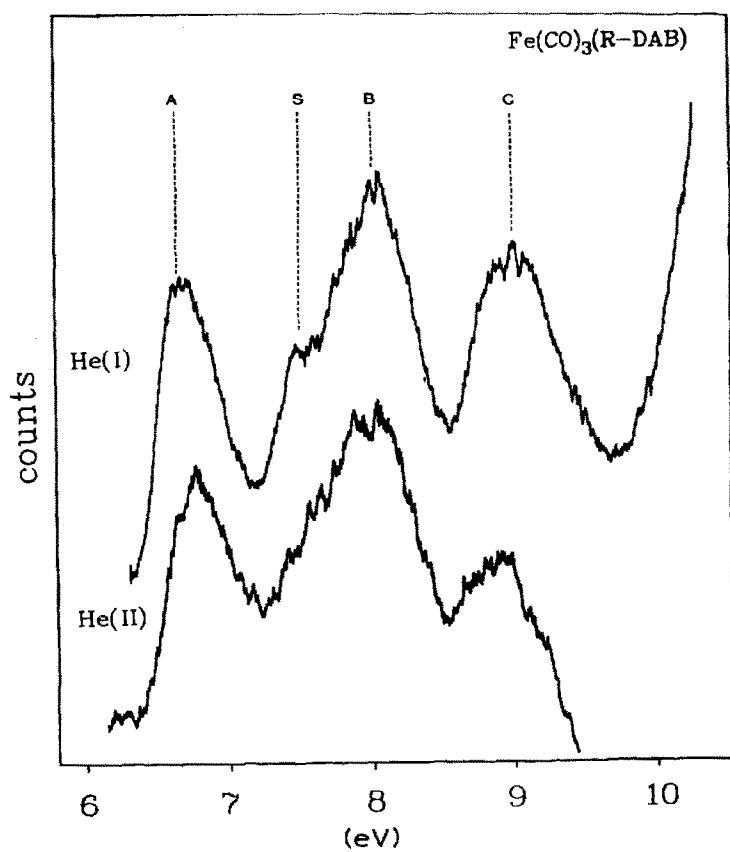
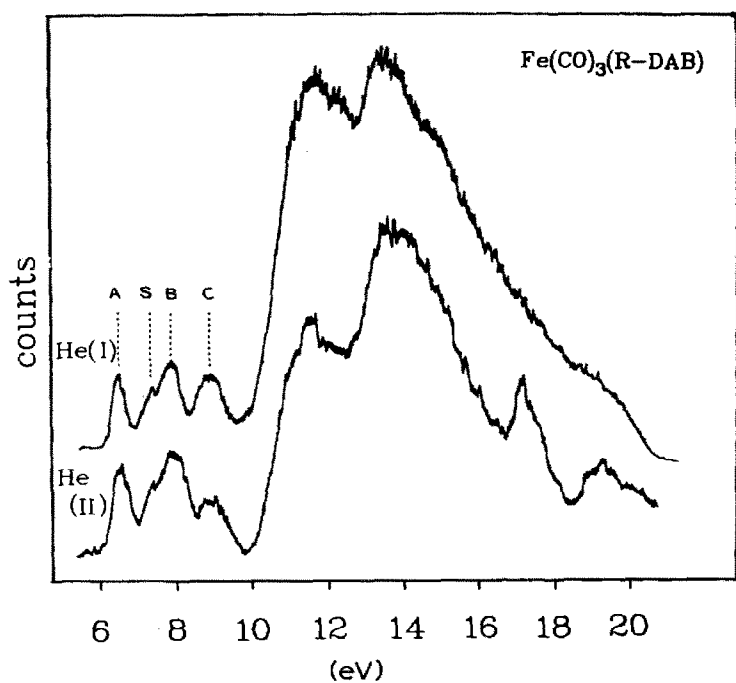


Fig. 6. Full (a) and expanded (b) He(I) and He(II) photoelectron spectra of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ ($\text{R} = \text{t-Bu}$).

TABLE 4

OBSERVED VERTICAL IONIZATION ENERGIES (eV) OF $[M(\text{CO})_3(\text{R-DAB}(\text{R}', \text{R}''))]$ AND FREE LIGAND R-DAB

M	R	R' = R''	IE (± 0.05 eV)			
			Band index			
			A	S	B	C
Fe	t-Bu	H	6.72	7.62	8.03 ^a	9.05 ^a
	c-Hex	H	6.58	7.49	7.79/7.94	8.85
	n-Bu	CH ₃	6.74	7.60	8.01	9.0 ^a
Ru	i-Pr ₂ CH	H	6.45		7.92	9.11
Assignment			$d + \pi_3^*$	$d + n_+$	$d_\pi + d_{z^2}$	n_+
$T_i(C_s)$			a'	a''	$a' + a'$	a'
i-Pr ₂ CH-DAB			9.3	9.5		
i-Pr-DAB [42]			9.5	9.8	11.7(sh)	
Assignment			$n_+, n_-, \pi_2(-)$		$\pi_1 + \sigma$	

^a Broad maximum.

During recent investigations of our group [15] on the electronic structure of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ in relationship to resonance Raman and MCD spectra, MO calculations have been performed by the CNDO/S method using the parametrization of Del Bene and Jaffé [22], in which the repulsion integrals were estimated by the method of Nishimoto and Mataga [38]. The final orbital interaction diagram is

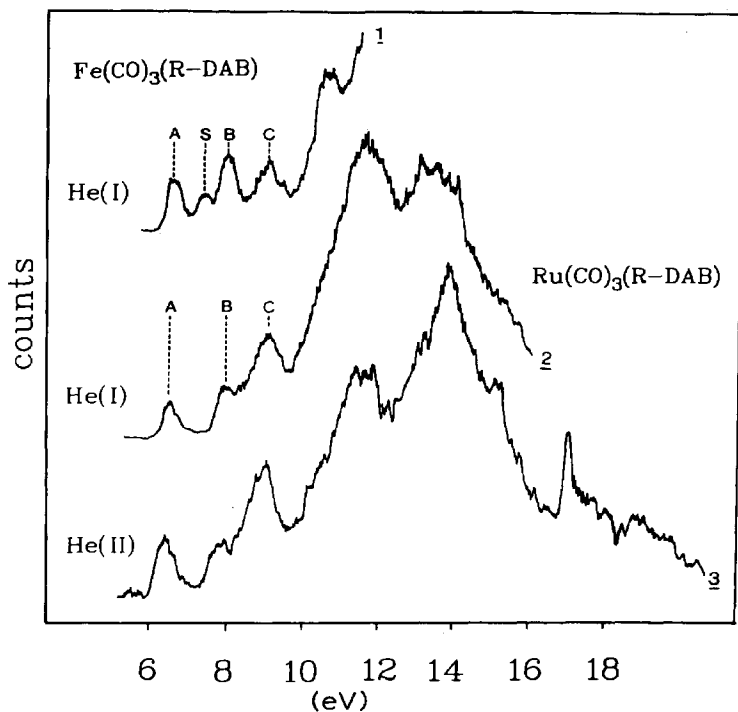


Fig. 7. A comparison between the He(I) photoelectron spectrum (1) of $[\text{Fe}(\text{CO})_3(\text{t-Bu-DAB})]$ and the He(I) and He(II) photoelectron spectra (2 and 3) of $[\text{Ru}(\text{CO})_3(\text{R-DAB})]$ (R = i-Pr₂CH).

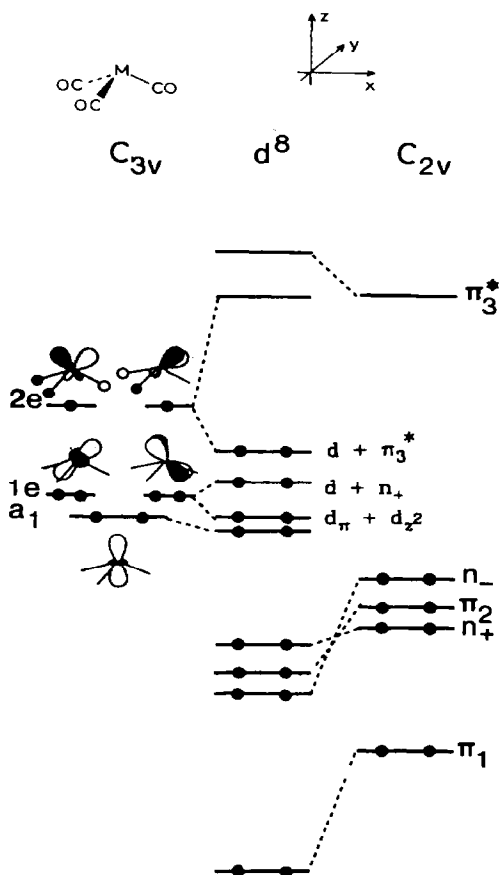


Fig. 8. Qualitative MO scheme of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$.

in agreement with the MO schemes for $[\text{Fe}(\text{CO})_3(\text{butadiene})]$ and $[\text{Fe}(\text{CO})_3(\text{cyclobutadiene})]$ given by Hoffmann and co-workers [24,39] and by Böhm and Gleiter [40]. The relevant part of the MO scheme is shown in Fig. 8.

With this in mind, the UP spectra of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ (Fig. 6a) can be assigned straightforwardly. The bands A, S and B at 6.58, 7.49 and 7.79–7.94 eV respectively, show hardly any decrease in intensity on going from He(I) to He(II) radiation, indicating metal d character (prob. > 50%). These bands with an intensity ratio in He(I) of about 1/1/2, belong to ionizations from $d + \pi_3^*$ (A), $d + n_+$ (S), d_π (B) and d_{z^2} (B). The orbital sequence of $d + n_+$ and d_π is tentative, because of the contradiction between results of electronic absorption and MCD spectra on the one hand and MO calculations [15] on the other. An argument for this orbital sequence can, however, be found by comparing the UP spectra of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$ with those obtained for $[\text{Fe}(\text{CO})_3(\text{R}_1\text{R}_2\text{-ABD})]$ ($\text{R}_1\text{R}_2\text{-ABD} = \text{R}_1\text{N}=\text{CHCH}=\text{CHR}_2$) in which band S is absent [41]. In this π -complex level interaction between a metal d and nitrogen lone pair orbital is impossible. Therefore it can be assumed that, by substitution of a 1-aza-1,3-butadiene ($\text{R}_1\text{R}_2\text{-ABD}$) by a 1,4-diaza-1,3-butadiene (R-DAB), band S arises from such a level interaction as a result of a different bonding mode and a second nitrogen atom. Another argument for assigning shoulder S to ionization from a $d + n_+$ orbital is the minor decrease of intensity on going to

He(II), which could be due to $N_{2s/2p}$ participation. Expanded spectra are shown in Fig. 6b to illustrate this phenomenon.

Band C is assigned to ionization from the symmetric nitrogen lone pair orbital n_+ (a') alone and not to n_- (a''), because of the large stabilization of the latter orbital. That this band does not belong to the $\pi_2(-)$ orbital has been confirmed by recording the UP spectra of the methyl substituted $[\text{Fe}(\text{CO})_3(\text{n-Bu-DAB}\{\text{Me,Me}\})]$. As can be seen from Table 4, band C is not destabilized by methyl substitution, and this is in line with the assignment of C to n_+ and not to $\pi_2(-)$. The ionization band of this latter orbital will be obscured by the broad band at higher energy.

The analogous complex $[\text{Ru}(\text{CO})_3(\text{R-DAB})]$ can only be isolated for R-DAB ligands containing very bulky R groups, such as Mes, *p*-Tol or *i*-Pr₂CH, at the coordinating N atoms. Of these, *i*-Pr₂CH is the only known alkyl R-DAB which forms a mononuclear ruthenium complex in the solid state [17]. The lowest *IE* of free *i*-Pr₂CH-DAB is more or less the same as that for *t*-Bu-DAB [10,3b] and *i*-Pr-DAB [42], namely 9.4 eV, corresponding to ionization from n_+ , $\pi_2(-)$ and n_- (see Table 4).

The first band (A) in the UP spectra of $[\text{Ru}(\text{CO})_3(\text{i-Pr}_2\text{CH-DAB})]$ is destabilized by 0.15 eV with respect to the first band of the iron complex. This lowering is an indication of less π -back-bonding into the π_3^* orbital in the case of Ru (Fig. 8). This difference in π -back-bonding is also evident from the increase in $\nu(\text{C}=\text{N})_s$ observed by Kokkes et al. [15] on going from Fe to Ru in $[\text{M}(\text{CO})_3(\text{R-DAB})]$.

With this in mind it is not surprising that the shoulder S, visible in the spectra of $[\text{Fe}(\text{CO})_3(\text{R-DAB})]$, has shifted underneath band B in the Ru analogue, since this complex will have a smaller level interaction between the n_+ and $d(a_1)$ levels. Band C at 9.11 eV is assigned to the n_+ lone pair combination of nitrogen, which is stabilized by about 0.20 eV with respect to the free ligand. This shift is the same as in the series $[\text{M}(\text{CO})_4(\text{R-DAB})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), and of the same order as observed for other $\text{Fe}(\text{CO})_3$ and $\text{Ru}(\text{CO})_3$ complexes [25,26].

It was not possible to obtain further information from the higher *IE* region because of the very complex σ -structure of the *i*-Pr₂CH-DAB ligand.

*d*¹⁰ Complexes

(i) $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$.

The expanded UP spectra of $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$ are presented in Fig. 9, and the data are listed in Table 5.

The valency of the Ni atom in $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$ is formally zero, as in $[\text{Ni}(\text{t-Bu-DAB})_2]$. For such *d*¹⁰ systems there are two possible structures, tetrahedral or square planar, of which the former is more likely and was the adopted geometry for $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$ [43]. However, it has been shown [44] that for R = aryl the R-DAB ligand in $[\text{Ni}(\text{R-DAB})_2]$ surround the Ni atom in a square planar manner, whereas for R = alkyl, (e.g. *c*-Hex) the ligands are orthogonal to each other, forming a tetrahedron due to steric repulsion [45].

The intensity ratio of the first two bands (A and B) in the UP spectra of $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$, at 6.84 and 7.65 eV respectively, is 3/2. Assuming that this complex also possesses a tetrahedral configuration, bands A and B arise simply from the ligand split metal *d* orbitals "*t*₂" and "*e*". The ligand field splitting parameter Δ'_l appears to be ca. 6450 cm⁻¹. Overlapping bands at higher energy are due to ionizations from ligand (n_+ , $\pi_2(-)$ at -9.5 eV) and CO (5σ , $1\pi + 4\sigma$) orbitals.

TABLE 5

OBSERVED VERTICAL IONIZATION ENERGIES (eV) OF $[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$ AND $[\text{M}(\text{t-Bu-DAB})_2]$ ($\text{M} = \text{Fe}, \text{Ni}$)

Compound	$IE (\pm 0.05 \text{ eV})$			
	Band index			
	A	B	Δ (cm^{-1})	C
$[\text{Ni}(\text{CO})_2(\text{t-Bu-DAB})]$	6.84	7.65	6450	9.5
$[\text{Ni}(\text{t-Bu-DAB})_2]$	5.8 ^a	8.01	17.700	
$[\text{Fe}(\text{t-Bu-DAB})_2]$	5.75	8.13	20.800	
Assignment (D_{2d})	$b_2 + a_1$ "e"	$b_1 + e$ " t_2 "	10 Dq	ligand (n_+)

^a Some broadening has been observed. ^b d^{10} for Ni^0 and d^8 for Fe^0 .

d^8 and d^{10} complexes (ii) $[\text{M}(\text{t-Bu-DAB})_2]$ ($\text{M} = \text{Fe}, \text{Ni}$)

As is known from X-ray studies, $[\text{Ni}(\text{R-DAB})_2]$ ($\text{R} = \text{alkyl}$) possesses a (pseudo-)tetrahedral coordination around the Ni^0 atom [43]. Assuming D_{2d} symmetry the Ni $3d^{10}$ orbitals transform as b_2, a_1 (e -like) and b_1, e (t_2 -like). According to CNDO/S [35] calculations and a qualitative MO scheme proposed by tom Dieck et al. [44], the σ -donation of the two R-DAB ligands occurs into empty Ni $4s$ and $4p$ orbitals. In this MO scheme a relatively large splitting of the t_2 -like d orbitals was assumed as the result of strong π -backbonding into empty $\pi^*(e)$ levels from the two orthogonal R-DAB π -systems. tom Dieck and co-workers have also measured the He(I) PE

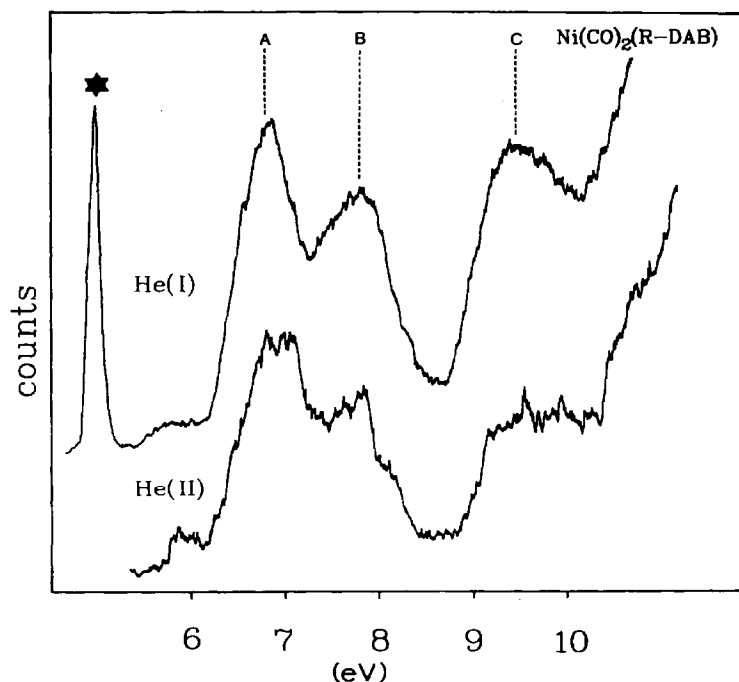


Fig. 9. Expanded He(I) and He(II) photoelectron spectra of $[\text{Ni}(\text{CO})_2(\text{R-DAB})]$ ($\text{R} = \text{t-Bu}$). Note: band marked with an asterisk arises from ionization of He by He(II) α radiation.

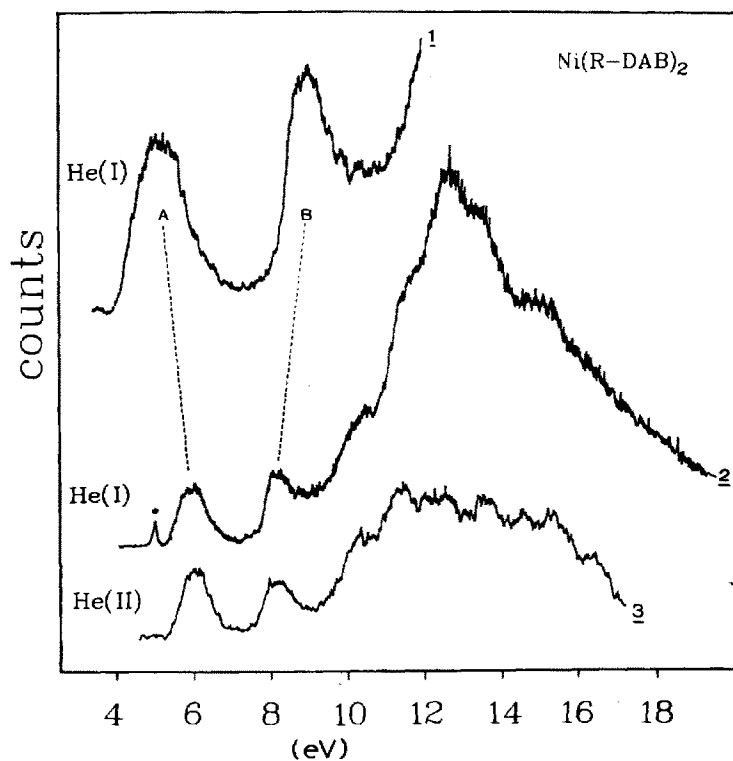


Fig. 10. Expanded He(I) (1), full He(I) (2) and He(II) (3) photoelectron spectra of $[\text{Ni}(\text{R-DAB})_2]$ ($\text{R} = t\text{-Bu}$).

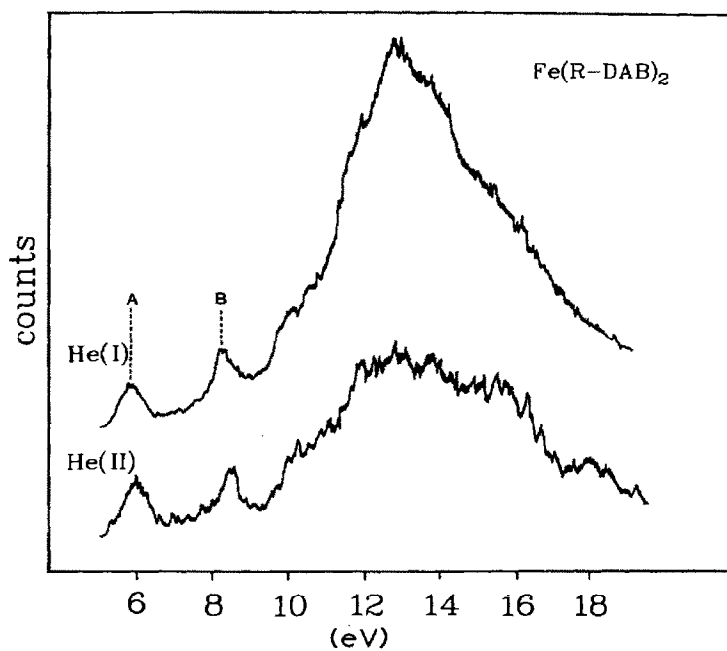


Fig. 11. He(I) and He(II) photoelectron spectra of $[\text{Fe}(\text{R-DAB})_2]$ ($\text{R} = t\text{-Bu}$).

TABLE 6

A COMPARISON BETWEEN THE MONONUCLEAR METAL CARBONYL AND R-DAB SUBSTITUTED COMPLEXES

		\overline{IE}_d (eV)		\overline{IE}'_d (eV)	ΔIE_d^a (eV)
d^6	[Cr(CO) ₆]	8.40	[Cr(CO) ₄ (R-DAB)]	6.86	-1.54
	[Mo(CO) ₆]	8.50	[Mo(CO) ₄ (R-DAB)]	6.96	-1.54
	[W(CO) ₆]	8.56	[W(CO) ₄ (R-DAB)]	7.00	-1.56
	[ReCl(CO) ₅]	9.23	[ReCl(CO) ₃ (R-DAB)]	7.76	-1.47
d^8	[Fe(CO) ₅]	9.25	[Fe(CO) ₃ (R-DAB)]	7.45	-1.80
d^{10}	[Ni(CO) ₄]	9.26	[Ni(CO) ₂ (R-DAB)]	7.16	-2.09
		\overline{IE}'_d		\overline{IE}''_d	
d^8	[Fe(CO) ₃ (R-DAB)]	7.45	[Fe(R-DAB) ₂]	6.94	-0.51
d^{10}	[Ni(CO) ₂ (R-DAB)]	7.16	[Ni(R-DAB) ₂]	6.68	-0.48

^a $\Delta IE'_d = \overline{IE}'_d - \overline{IE}_d$ or $\overline{IE}''_d - \overline{IE}'_d$.

spectrum of [Ni(R-DAB)₂], and have assigned the first *IE* at ~ 6 eV to metal *d* ionizations [43].

In the figures 10 and 11 are shown the low *IE* regions of the He(I) and He(II) spectra of [Ni(t-Bu-DAB)₂] and [Fe(t-Bu-DAB)₂], and the observed vertical *IE*'s are listed in Table 5.

Up to now we have discussed the electronic structures of transition metal carbonyl R-DAB complexes in which, as has been pointed out for [Ni(CO)₂(t-Bu-DAB)] (vide supra), a strong π -back-bonding can occur into the π^* CO. It is not surprising that replacement of the two carbonyl groups of [Ni(CO)₂(R-DAB)] by another R-DAB system causes an increase of electron density at the Ni atom. The assignment of the two weak bands in the UP spectra of [Ni(t-Bu-DAB)₂] is based on the intensity ratio in the He(II) spectra (use of the He(I) data is inadvisable, because of significant σ -ghosting). The ratio of 3/2 (A/B), supports the assignment of band A at 5.8 eV and B at 8.01 eV to ionization from the *t*₂-like (*e* + *b*₁) and *e*-like (*a*₁, *b*₂) orbitals respectively. In this case the ligand field splitting parameter Δ of 17.700 is much larger than that for [Ni(CO)₂(t-Bu-DAB)].

The electron density at the Ni atom is somewhat larger in [Ni(t-Bu-DAB)₂] than in [Ni(CO)₂(t-Bu-DAB)]; the values are 6.68 and 6.96 eV respectively. With this in mind it is not difficult to interpret the UP spectra (Fig. 11) of the pyrophoric 16e complex [Fe(t-Bu-DAB)₂], which also has a tetrahedral configuration around Fe⁰ *d*⁸ atom. Again two bands (A + B) are observed, at 5.75 and 8.13 eV, respectively. The latter band is artificially raised in intensity due to the large σ -ghosting underneath. On changing to He(II) radiation the intensity ratio of A/B becomes about 1/1, consistent with a *d*⁸ tetrahedral ligand field splitting of the Fe 3*d* orbitals: *b*₂ + *a*₁ ("e²") and at lower *IE* *b*₁ + *e* ("t₂⁴"). For this complex Δ is 20.800 cm⁻¹.

Correlation *d*⁶-*d*⁸-*d*¹⁰ complexes

Now that the *d* orbitals have been assigned it is possible to correlate the weighted

average IE 's of the transition metal d orbitals of the mono-substituted complexes (\overline{IE}'_d) with those of the unsubstituted carbonyl (\overline{IE}_d) and to study the influence of R-DAB on the metal centres.

As can be seen from Table 6, the values of $\Delta IE_d (= \overline{IE}'_d - \overline{IE}_d)$ are negative, and the absolute values increase on going from d^6 [$M(\text{CO})_4(\text{R-DAB})$]-[$M(\text{CO})_6$] ($M = \text{Cr, Mo, W}$) (-1.52 eV), d^8 [$M(\text{CO})_3(\text{R-DAB})$]-[$M(\text{CO})_5$] ($M = \text{Fe}$) (-1.80 eV) to d^{10} [$M(\text{CO})_2(\text{R-DAB})$]-[$M(\text{CO})_4$] ($M = \text{Ni}$) (-2.09 eV). The decreasing ΔIE_d in this series, resulting directly from replacement of two CO groups by one R-DAB fragment, indicates an increasing electron density on the transition metal centre. The value of $\Delta \overline{IE}_d$ increases on going from d^6 to d^{10} as a result of the smaller number of CO's left in the molecule. Surprisingly the difference between the $\Delta \overline{IE}_d$ values for the d^6 and d^8 series (0.26 eV) is virtually the same as that between the d^8 and d^{10} series (0.29 eV). Further replacement of the CO's by another R-DAB in the case of d^8 [$\text{Fe}(\text{R-DAB})_2$] and d^{10} [$\text{Ni}(\text{R-DAB})_2$] induces in even more electron density on the metal centre, but less than in the mono-R-DAB complexes: ΔIE_d 0.48 eV.

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